

# Charge ordering and opening of spin gap in $\text{NaV}_2\text{O}_5$

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We suggest that the phase transition observed in  $\text{NaV}_2\text{O}_5$  at  $T = 34\text{K}$  is not a spin-Peierls transition, but a charge ordering transition, related to the formal presence in this system of equal number of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions. Below  $T_c$ ,  $\text{V}^{4+}$  ions form a zigzag structure, which is consistent with the experimentally observed doubling of the lattice period in  $a$  and  $b$  directions. We show that this charge ordering also results in the alternation of spin exchange constants along the  $b$ -direction, which opens a gap in the spin excitation spectrum. We emphasize the role of lattice distortions around V ions both in the formation of the charged ordered state and in the spin-gap opening.

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In this paper we discuss the interplay between charge and spin degrees of freedom in  $\text{NaV}_2\text{O}_5$ , which initially was identified as an inorganic spin-Peierls (SP) material similar to  $\text{CuGeO}_3$ . Indeed, according to the first X-ray studies of this compound [1]  $\text{V}^{4+}$  ions form spin- $\frac{1}{2}$  chains, which are separated from each other by nonmagnetic  $\text{V}^{5+}$ -chains. Below  $T_c = 34\text{K}$ , magnetic susceptibility, X-ray and neutron scattering measurements indicate the opening of a spin gap accompanied by doubling of the lattice period in the chain direction [2–4].

However, the situation in  $\text{NaV}_2\text{O}_5$  is evidently more complicated and more interesting than in conventional SP systems. First of all, the original crystal structure was recently questioned [5–7]. According to the new X-ray and neutron data, the structure of  $\text{NaV}_2\text{O}_5$  was identified as a centrocymetric group  $Pmmn$ , in contrast to the earlier assignment  $P2_1mn$  [1]. The new structure implies that all V sites are equivalent. As an average valence of V in  $\text{NaV}_2\text{O}_5$  is 4.5+, there is one  $d$ -electron per two equivalent V ions, which makes the description of this compound as a spin- $\frac{1}{2}$  chain material not obvious.

Other indications that the physics of  $\text{NaV}_2\text{O}_5$  may be different from that of, e.g.,  $\text{CuGeO}_3$  come from thermodynamic data. In particular, the study of specific heat [8] shows that the entropy of the transition in  $\text{NaV}_2\text{O}_5$  is larger than the entropy of a pure SP system. The ratio  $\frac{2\Delta_0}{T_c}$ , where  $\Delta_0$  is the value of the spin gap at  $T = 0$ , is for  $\text{NaV}_2\text{O}_5 \sim 6$  – much larger than for the known SP materials, where it is close to 3.5, which follows from the weak-coupling mean field theory of SP transition [10]. Another evidence that the phase transition in  $\text{NaV}_2\text{O}_5$  may be of different nature comes from a rather weak dependence of  $T_c$  on magnetic field: the shift of  $T_c$  is  $\sim 5$  times smaller [8,9] than the theoretical predictions [10,11]. Yet another spectacular difference in the behavior of  $\text{NaV}_2\text{O}_5$  and  $\text{CuGeO}_3$  is the temperature-dependence of the thermal conductivity [12]: below  $T_c$  the thermal conductivity of  $\text{NaV}_2\text{O}_5$  increases by a factor of 5, while in  $\text{CuGeO}_3$  the corresponding anomaly is very weak.

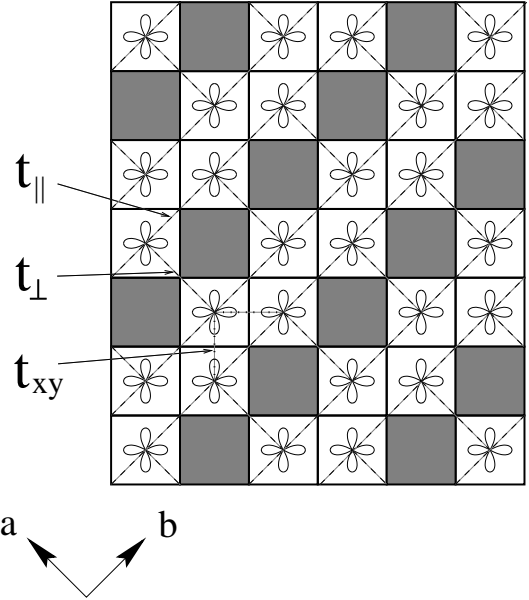


FIG. 1. Schematic representation of the crystal structure of V-O plane of  $\text{NaV}_2\text{O}_5$ . Oxygens are located at the corners of plaquettes and vanadium ions are located at their centers; the shaded plaquettes are vacant. Also shown are the relevant  $d_{xy}$ -orbitals of V ions and vanadium ladders (dashed lines).

All these facts show that the phase transition in  $\text{NaV}_2\text{O}_5$  is not an ordinary SP transition. We suggest below that the main phenomenon responsible for the transition is, in fact, a charge ordering (CO), related to the formal presence in this system of equal number of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions. While at high temperature there is a rapid oscillation between the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  states, so that on the time scale larger than the electron hopping time all V ions look equivalent ( $\text{V}^{4.5+}$ ), at low temperature a CO transition, similar to the Verwey transition in  $\text{Fe}_3\text{O}_4$  [13], occurs. The opening of a spin gap, accompanying this transition, is just one of the consequences of the charge ordering. The appearance below  $T_c$  of two inequivalent V sites, which were crudely identified as  $\text{V}^{4+}$  and  $\text{V}^{5+}$ , was indeed observed in the recent NMR experiment [14].

However, the detailed nature of this CO and its relation to the opening of the spin gap remains still unclear. Elucidation of this relation is the main subject of this paper.

The structure of  $\text{NaV}_2\text{O}_5$  consists of  $\text{V}_2\text{O}_5$  layers with approximately square oxygen lattice. Two third of the oxygen plaquettes are occupied by V ions located in the middle of the plaquettes (see Fig. 1). Due to details of the crystal structure, only one of the three  $t_{2g}$ -orbitals of V, namely the  $d_{xy}$ -orbital, is occupied [5]. As the  $d$ - $d$  hopping goes mainly via intermediate oxygens, the diagonal (or next-nearest-neighbor (nnn)) hopping amplitudes,  $t_\perp$  and  $t_\parallel$ , are much larger than the nearest-neighbor (nn) hopping amplitude  $t_{xy}$ , which makes  $\text{NaV}_2\text{O}_5$  a quarter-filled system of vanadium two-leg ladders (See Fig. 1). Tight binding fitting of the LDA band structure gives  $t_\perp \sim 0.35\text{eV}$ ,  $t_\parallel \sim 0.15\text{eV}$ , and  $t_{xy} \sim 0.012\text{eV}$  [5], all remaining hopping amplitudes being much smaller. Using the empirical Harrison rules Horsh and Mack obtained similar values for  $t_\perp$  and  $t_\parallel$ , but a much larger  $t_{xy} \sim 0.3\text{eV}$  [15].

With the parameters of Ref. [5] one can understand the one-dimensional spin structure of  $\text{NaV}_2\text{O}_5$ . Each rung is occupied by a single electron in a bonding state with the energy  $-t_\perp$ . For strong on-site Coulomb repulsion the energy cost of electron transfer on a neighboring rung is (at least)  $2t_\perp$ . For  $2t_\perp > 4t_\parallel$  the electron hopping between rungs is energetically unfavorable and can occur only virtually. Thus, although the charge degrees of freedom are not frozen and all V ions are equivalent, the system remains insulating. In Refs. [5,15]  $\text{NaV}_2\text{O}_5$  was described as an effective spin system with spins being localized on the rungs of vanadium ladders (instead of vanadium sites). As the spin-exchange between electrons of neighboring ladders is weak [5,15], the spin system is quasi-one-dimensional (each ladder corresponding to a spin chain).

In this paper we go beyond the decription of  $\text{NaV}_2\text{O}_5$  as a spin-chain material and include also the charge dynamics. We start from the electronic Hamiltonian, which includes the electron hopping in ladders (with the amplitudes  $t_\perp$  and  $t_\parallel$ ) and between ladders (with the amplitude  $t_{xy}$ ) [see Fig. 1], as well as the Coulomb interaction between electrons on different V sites: the on-site Coulomb repulsion  $U$  is the largest parameter and is here taken infinite, the nn interaction  $V_2$  (e.g., between sites C and D on neighboring ladders [see Fig. 3]), the nnn interaction  $V_1$  inside ladders (e.g., between sites A and E or B and E [see Fig. 3]), etc.

Next we make a projection on the subspace of states with one electron per rung. Four different states of a single electron on a rung can be represented as the eigenstates of spin  $S = \frac{1}{2}$  and isospin  $T = \frac{1}{2}$  operators,  $|\frac{1}{2}S^z\rangle \otimes |\frac{1}{2}T^z\rangle$ , where  $T^z = \pm\frac{1}{2}$  corresponds to an upper/lower position of the electron on a rung (see Fig. 3).

The effective spin-isospin Hamiltonian can then be written in the form:

$$H = H_0 + H_1. \quad (1)$$

Here,  $H_0$  is a pure isospin Hamiltonian:

$$H_0 = -2t_\perp \sum_{\mathbf{r}} T_{\mathbf{r}}^x + 2V_1 \sum_{\mathbf{r}} \left( T_{\mathbf{r}}^z T_{\mathbf{r}+\mathbf{b}}^z + \frac{1}{4} \right) + 2V_2 \sum_{\langle \mathbf{r}_1 \mathbf{r}_2 \rangle} \left( \frac{1}{4} - T_{\mathbf{r}_1}^z T_{\mathbf{r}_2}^z \right) + H'_0, \quad (2)$$

where the vector  $\mathbf{r}$  runs over the sites of an effective lattice located on the rungs of V ladders. The first term in Eq.(2) describes the electron hopping in the rungs, the second term is the nnn Coulomb interaction between electrons occupying neighboring rungs  $\mathbf{r}$  and  $\mathbf{r} + \mathbf{b}$  of a ladder ( $\mathbf{b}$  is a unit lattice vector in the ladder direction), the third term is the repulsion between nn electrons from neighboring ladders and  $H'_0$  stands for all other interaction terms (the longer range Coulomb terms, the interaction via the lattice, etc.).

The Hamiltonian  $H_1$  in Eq.(1) describes the interaction between spin and isospin degrees of freedom. The strongest spin-isospin interaction occurs inside ladders. The corresponding Hamiltonian for a single ladder has the form:

$$H_{ST} = -\frac{4t_\parallel^2}{\Delta} \sum_n \left[ \left( \frac{1}{4} - \mathbf{S}_n \cdot \mathbf{S}_{n+1} \right) \left( \frac{1}{4} + \mathbf{T}_n \cdot \mathbf{T}_{n+1} - 2T_n^z T_{n+1}^z \right) + \left( \frac{3}{4} + \mathbf{S}_n \cdot \mathbf{S}_{n+1} \right) \left( \frac{1}{4} - \mathbf{T}_n \cdot \mathbf{T}_{n+1} \right) \right], \quad (3)$$

where  $n$  runs over rungs of the ladder.

The Hamiltonian Eq.(3) originates from the virtual electron hopping between two neighboring rungs of a ladder and  $\Delta$  is the increase of energy due to electron transfer on the neighboring rung. The value of  $\Delta$  is determined by the isospin Hamiltonian  $H_0$  and depends on a state considered. If, for instance, we neglect the Coulomb terms in the disordered phase, then  $\Delta = 2t_\perp$ , while for the extreme zigzag CO discussed below:  $\Delta \sim 2V_1$ . Note, that in the  $U \rightarrow \infty$  limit  $\Delta$  is finite. Since the hopping between ladders,  $t_{xy}$ , is much smaller than  $t_\perp$  and  $t_\parallel$  [5], we ignored the corresponding contributions to  $H_1$ .

The spin-isospin structure of the exchange interaction is a consequence of the Pauli principle: the wave function of two neighboring electrons in the intermediate state (when they occupy the same rung) should be antisymmetric under exchange of both their spin and isospin coordinates. Therefore, if the total spin of two electrons on neighboring rungs,  $\mathbf{S} = \mathbf{S}_n + \mathbf{S}_{n+1}$ , is zero (i.e., the spin state is antisymmetric), the isospin state of these electrons has to be symmetric:  $T = 1$ , where  $\mathbf{T} = \mathbf{T}_n + \mathbf{T}_{n+1}$ , and, vice versa, if  $S = 1$ , then  $T = 0$ . Correspondingly, the first term in square brackets of Eq. 3 is the projection operator on  $S = 0$ ,  $T = 1$ ,  $T^z = 0$  state, while the second term is the projection operator on  $S = 1$ ,  $T = 0$  state.

The projection of the total isospin of two electrons,  $T^z$ , in both terms is zero, because we assumed the on-site Coulomb repulsion  $U$  to be infinitely large, so that the hopping between rungs is only possible if electrons are located on different chains of the ladder.

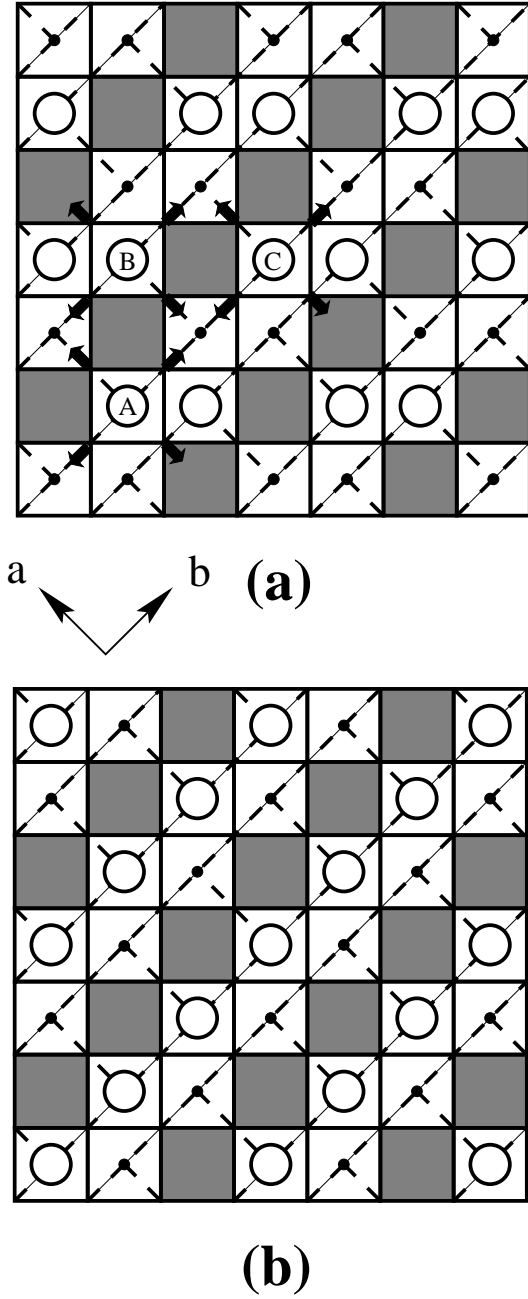


FIG. 2. Two types of CO: the zigzag structure (a) and the old structure, in which  $V^{4+}$  chains are separated by  $V^{5+}$  chains (b). Large circles denote  $V^{4+}$  ions with a large ionic radius, while small circles denote small nonmagnetic  $V^{5+}$  ions. Arrows denote shifts of oxygen atoms around  $V^{4+}$  ions in one ladder (for simplicity, the shifts induced by  $V^{4+}$  ions in other ladders are not shown).

Since  $H_1$ , resulting from the virtual hopping between rungs, is smaller than  $H_0$ , we can start by considering

only the charge degrees of freedom first. The isospin Hamiltonian  $H_0$  describes the competition between the hopping along rungs, which tends to make V ions equivalent, and the Coulomb interaction, which favors a CO. If, for instance, we leave only the first two terms in Eq.(2), then the ladders become decoupled and the Hamiltonian of each ladder is the Hamiltonian of the Ising model in perpendicular magnetic field. For  $V_1 < 2t_\perp$  its ground state is disordered (all vanadium ions are equivalent), while in the opposite case, isospins in the ground state are ordered antiferromagnetically:  $\langle 2T_n^z \rangle = \eta(-1)^n$ . This CO corresponds to the zigzag occupation of vanadium sites by electrons as shown in Fig. 2a, where the large circles denote  $V^{4+}$  ions with a large ionic radius, while small circles denote small nonmagnetic  $V^{5+}$  ions. (Of course, if the ladders would be really decoupled, the sign of the order parameter in each ladder is arbitrary.)

On the other hand, the third term in Eq.(2) favors the structure shown in Fig. 2b, which would give one-dimensional spin chains of  $V^{4+}$  ( $d^1$ ,  $S = \frac{1}{2}$ ) ions and is the initially assumed crystal structure [1]. If we would take into account only the second and the third terms with  $V_2 = \sqrt{2}V_1$ , the zigzag structure (Fig. 2a) would have lower energy than the chain structure (Fig. 2b). Of course, it is necessary to include all longer range Coulomb interactions to find the real ground state of the system. The calculation of the Madelung energies of these two-dimensional structures shows, that they are rather close, the chain structure of Fig. 2b being slightly more favorable.

There is, however, another type of interaction between charges – the interaction via lattice distortions, which, unlike the Coulomb interaction, is local. As shown in Fig. 2a, this latter interaction definitely favors the zigzag structure: large  $V^{4+}$  ions push out neighboring oxygens (the directions of oxygen displacements in a ladder are shown in Fig. 2a by arrows). As a result, neighboring plaquettes in a ladder would preferably be occupied by smaller  $V^{5+}$  ions. Roughly speaking, the lattice relaxation around empty and occupied vanadium ions enhances the nnn repulsion, which favors the zigzag ordering.

Note, that the zigzag structure shown in Fig. 2a immediately gives us a new periodicity with the doubling of periods along both  $a$  and  $b$  directions, in accordance with the experiment [3]. Thus, one does not need to invoke the SP mechanism to explain the distortion pattern observed below  $T_c$ . We also note, that there exist four equivalent realizations of the zigzag structure of Fig. 2a, which differ by the location and orientation of pairs of nn  $V^{4+}$  ions (large circles in Fig. 2a). This may provide a clue to understanding of the four-fold increase of the period in  $c$ -direction below  $T_c$  [3].

The smallness of  $T_c = 34K$  in  $\text{NaV}_2\text{O}_5$  as compared to the parameters of the Hamiltonian (2) (e.g.,  $t_\perp$ ,  $V_1$ ) may be explained by the competition between the electron

hopping and the electron-electron interactions, which reduces the gap in the spectrum of isospin excitations. If, again, we would leave only the first two terms in the Hamiltonian (2), the gap equals  $|2t_{\perp} - V_1|$ . Although these excitations do not carry charge, they can be excited by an electric field applied perpendicularly to ladders (i.e., in  $a$ -direction), which may explain why the continuum of relatively low-energy excitations, observed in the infrared absorption experiments, disappears when the orientation of the electric field is changed from  $a$ -direction to  $b$ -direction. [16]. The repulsion between electrons from neighboring ladders (the third term in Eq.(2)) frustrates the zigzag structure, which results in additional reduction of  $T_c$ .

Next we consider the spin excitations. From Eq.(3) the effective spin-exchange constant in the chain direction,  $J_{\parallel}$ , is

$$J_{\parallel} = \frac{4t_{\parallel}^2}{\Delta} \langle \mathbf{T}_n \cdot \mathbf{T}_{n+1} - T_n^z T_{n+1}^z \rangle = \frac{4t_{\parallel}^2}{\Delta} \langle T_n^x T_{n+1}^x + T_n^y T_{n+1}^y \rangle. \quad (4)$$

where  $\langle \dots \rangle$  denotes the thermal and quantum average.

From Eq.(4) it is obvious that CO would decrease the effective spin-exchange constant  $J_{\parallel}$ . In particular, if the electrons in neighboring rungs  $n$  and  $n+1$  of a ladder are completely uncorrelated,  $\langle T_n^x T_{n+1}^x + T_n^y T_{n+1}^y \rangle = \frac{1}{2}$ , while for the extreme zigzag charge ordering ( $\langle 2T_n^z \rangle = (-1)^n$ ):  $\langle \mathbf{T}_n \cdot \mathbf{T}_{n+1} - T_n^z T_{n+1}^z \rangle = 0$  and the spin-exchange constant is zero. In general, the charge order parameter  $\eta$  does not have the maximal amplitude, so that CO would result only in a partial reduction of  $J_{\parallel}$ . According to Eq.(4), the spin stiffness in the chain direction becomes smaller as temperature decreases, which could be observed in neutron scattering experiments.

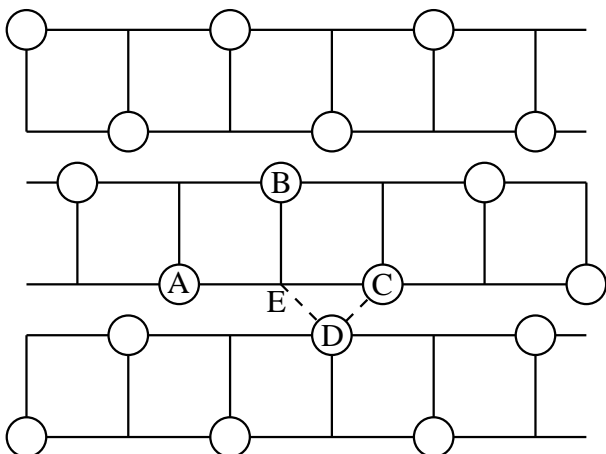


FIG. 3. This figure demonstrates that the zigzag CO makes the spin-exchange in neighboring pairs of electrons ( $AB$  and  $BC$ ) inequivalent. The inequivalence is caused by the difference in the occupation of V sites in neighboring ladders.

More importantly, the zigzag charge ordering opens

a spin gap, which in this picture is a secondary effect. There are, in principle, two scenarios for the spin gap opening. First, as one can see from Fig. 2a, the CO results in the appearance of pairs of nn vanadiums coupled by the hopping amplitude  $t_{xy}$ , [cf. Fig. 1]. For large  $t_{xy}$  these interladder pairs would form spin singlets, which could explain the spin gap in  $\text{NaV}_2\text{O}_5$  [17]. However, we think that this is rather unlikely. On the one hand, as we mentioned above, the band structure calculations give rather small value of  $t_{xy} \sim 0.012\text{eV}$  [5]. On the other hand, even with larger  $t_{xy}$  (as, e.g., in Ref. [15]) there are several competing mechanisms of nn exchange: an antiferromagnetic one, due to direct d-d overlap and an exchange via  $90^\circ$  V-O-V path, which according to Goodenough-Kanamori-Anderson rule is ferromagnetic. Even the sign of the resulting interaction is unclear: Horsh and Mack obtained a small antiferromagnetic nn exchange [15], while the LDA+U calculations for the structurally similar material  $\text{CaV}_2\text{O}_5$  give a ferromagnetic nn interaction [18]. Furthermore, in  $\text{NaV}_2\text{O}_5$  there is a third mechanism of exchange resulting from the circular motion of electrons over V-V-V triangles (e.g., along the CDE triangle in Fig. 3). The sign of the latter exchange coincides with the sign of the product of three amplitudes of electron hopping along the sides of a triangle [cf. [19]]. As the latter sign is negative [5], the corresponding spin-exchange is ferromagnetic.

Thus, whether the interladder singlets are formed or not, is still not clear. It is, however, obvious that the zigzag CO results in an alternation of the exchange constants *along* the spin chains formed by vanadium ladders. Indeed, the exchange interaction between the ions A and B (see Fig. 3) goes via a plaquette having  $V^{5+}$  both above and below it, whereas for B and C ions the corresponding positions are occupied by  $V^{4+}$  ions. This inequivalence in the occupation of V sites in neighboring ladders produces a difference in the shifts of the corresponding oxygen and vanadium ions, thereby affecting the electron hopping amplitudes and, ultimately, resulting in the alternation of the exchange constants along the ladder direction,

$$J_{\parallel}(n, n+1) = J_{\parallel}(1 + (-1)^n \delta), \quad (5)$$

which opens the spin gap  $\sim \frac{\delta^{2/3}}{\sqrt{|\ln \delta|}}$ . The detailed calculation of the alternation amplitude  $\delta$  induced by the CO is a formidable problem requiring the knowledge of the shifts of oxygen and vanadium ions, the modification of electron transfer energies, etc. One can, however, easily see, that  $\delta$  is a linear function of the charge order parameter  $\eta = (-1)^n \langle 2T_n^z \rangle$ , so the temperature behavior of the spin gap is quite similar to that in SP systems, where  $\delta$  is proportional to the amplitude of the lattice distortion (unless, of course, the CO transition is of the first order).

Though the opening of the spin gap is not the main driving force of the transition, it also contributes to the

stabilization of the charge ordered phase. It may, in particular, be important in determining the relative phases of charge order parameter  $\eta$  in different ladders. If, for instance, for the phase of the charge order in the bottom ladder in Fig. 3 would be opposite, there would no doubling of the periodicity in  $a$ -direction and no alternation in the spin-exchange constants along the ladders, and consequently, no spin gap. The energy gain due to spin-gap opening, by itself, can make the structure of Fig. 2a more stable than the zigzag structure without the dimerization along  $a$ -axis.

Summarizing, we have shown that the very chemical composition of  $\text{NaV}_2\text{O}_5$  – the presence of one electron per two vanadium sites – rather naturally leads to a charge ordering at low temperatures. We argued, that in the ordered phase the occupied vanadium sites form zigzags. This CO is driven by the direct Coulomb repulsion and, most importantly, by the interaction with the lattice distortions. The CO results in the doubling of the lattice period both in  $a$  and  $b$  directions in agreement with experiments. Another consequence of the CO is the alternation of the exchange interaction along  $b$ -direction (along vanadium ladders), which opens a spin gap. Although the coupling between spin and charge degrees of freedom may also contribute to the charge ordering, the spin-gap opening is a consequence of the charge ordering. This picture is consistent with experimental observations for  $\text{NaV}_2\text{O}_5$ .

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*Note added:* After completion of this work two preprints appeared [20,21] in which similar ideas were put forward. Thalmeier and Fulde [21] argued in favor of the CO shown in Fig. 2b, after which they still had to invoke the spin-lattice coupling to get second transition of a spin-Peierls type. Experimentally two close phase transitions were observed in some samples of  $\text{NaV}_2\text{O}_5$  [22] but not in others [9]. Furthermore, when two transitions are observed, their temperature shifts, essentially, in the same way with magnetic field [8]. Thus, it may well be that these multiple transitions originate from the inhomogeneity of some samples, although this question definitely deserves further study. However, as we argued above, the zigzag structure of Fig. 2a seems to us much more favorable. Besides, in the model of Ref. [21] one completely ignores the largest electron hopping amplitude  $t_\perp$ , which would result in the random exchange between electron spins above  $T_c$ , instead of the quasi-one-dimensional behavior.

The results of Seo and Fukuyama [20] are closer to

ours; they also concluded that the zigzag structure is more favorable. Their arguments, however, are based on nn and nnn Coulomb terms only, which is definitely insufficient for the Coulomb interaction (as we mentioned above, the *long range* Coulomb interaction seems to favor the  $\text{V}^{4+}\text{-V}^{5+}$  chain structure). Furthermore, their singlets are formed by nearest-neighbor pairs between ladders, which, as we argued above, is rather questionable.

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